



## Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions

O. Vesna, S. Sjogren, E. Weingartner, V. Samburova, M. Kalberer, H. W. Gäggeler, M. Ammann

### ► To cite this version:

O. Vesna, S. Sjogren, E. Weingartner, V. Samburova, M. Kalberer, et al.. Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions. *Atmospheric Chemistry and Physics Discussions*, 2007, 7 (6), pp.15651-15668. hal-00303164

**HAL Id: hal-00303164**

**<https://hal.science/hal-00303164>**

Submitted on 7 Nov 2007

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Fatty acid aerosol  
hygroscopicity  
induced by  
ozonolysis**

O. Vesna et al.

# Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions

**O. Vesna<sup>1,2</sup>, S. Sjogren<sup>3</sup>, E. Weingartner<sup>3</sup>, V. Samburova<sup>4</sup>, M. Kalberer<sup>4</sup>,  
H. W. Gäggeler<sup>1,2</sup>, and M. Ammann<sup>1</sup>**

<sup>1</sup>Laboratory of Radio- and Environmental Chemistry, Paul Scherrer Inst., Villigen, Switzerland

<sup>2</sup>Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland

<sup>3</sup>Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Villigen, Switzerland

<sup>4</sup>Institute of Organic Chemistry, ETH Zürich, Zürich, Switzerland

Received: 1 October 2007 – Accepted: 24 October 2007 – Published: 7 November 2007

Correspondence to: M. Ammann (markus.ammann@psi.ch)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

Unsaturated fatty acids are important constituents of the organic fraction of atmospheric aerosols originating from biogenic or combustion sources. Oxidative processing of these may change their interaction with water and thus affect their effect on climate. The ozonolysis of oleic and arachidonic acid aerosol particles was studied under humid conditions in a flow reactor at ozone exposures close to atmospheric levels, at concentrations between 0.5 and 2 ppm. While oleic acid is a widely used proxy for such studies, arachidonic acid represents polyunsaturated fatty acids, which may decompose into hygroscopic products. The hygroscopic (diameter) growth factor at 93% relative humidity (RH) of the oxidized arachidonic particles increased up to 1.09 with increasing RH during the ozonolysis. In contrast, the growth factor of oleic acid was very low (1.03 at 93% RH) and was almost invariant to the ozonolysis conditions, so that oleic acid is not a good model to observe oxidation induced changes of hygroscopicity under atmospheric conditions. We show for arachidonic particles that the hygroscopic changes induced by humidity during ozonolysis are accompanied by about a doubling of the ratio of carboxylic acid to aliphatic functional groups. We suggest that, under humid conditions, the reaction of water with the Criegee intermediates might open a pathway for the formation of smaller acids that lead to more significant changes in hygroscopicity. Thus the effect of water to provide a competing pathway during ozonolysis observed in this study should be motivation to include water, which is ubiquitously present in and around atmospheric particles, in future studies related to aerosol particle aging.

## 1 Introduction

Atmospheric aerosols consist of both inorganic and organic compounds. Field measurements indicate that the organic fraction of atmospheric aerosols is in the range from 20 to 90%, depending on the location and sources (Kanakidou et al., 2005; Ja-

ACPD

7, 15651–15668, 2007

### Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

cobson et al., 2000; Novakov and Penner, 1993; Seinfeld and Pandis, 1998). Fatty acids, i.e., n-alkanoic and n-alkenoic acids, can make up a significant contribution to the organic fraction, they have been found in emissions from biomass burning (Oros and Simoneit, 2001), coal burning (Oros and Simoneit, 2000), fossil fuel combustion (Rogge et al., 1993), cooking (Rogge et al., 1991; Schauer et al., 1999), plants of the terrestrial biosphere (Cheng et al., 2004; Simoneit et al., 1988; Simoneit and Mazurek, 1982), and also in marine aerosols, where they are associated with sea salt aerosol and stem from degradation of marine biota (Mochida et al., 2002; Tervahattu et al., 2002). In all these sources, a significant fraction of fatty acids are unsaturated alkenoic acids (Kawamura and Gagosian, 1987; Wang et al., 2006). Some of these are polyunsaturated fatty acids, i.e., have more than one double bond, and their concentration may exceed the concentrations of monounsaturated fatty acids (Polzer and Bachmann, 1991). Given their amphiphilic nature, fatty acids can be considered as potentially important aerosol surfactants (Ellison et al., 1999; Tervahattu et al., 2002).

Processing of organic particulate matter by oxidants in the atmosphere is believed to significantly contribute to aerosol hygroscopicity and CCN activity that in turn influence the direct and indirect aerosol effects on the Earth's radiation balance (Kanakidou et al., 2005). A number of studies suggested the importance of the transformation of fatty acid surfactants by oxidative processing (Ellison 1999; Finlayson-Pitts, 1999). Thereby, the organic layer can be transformed from an inert, hydrophobic film to a reactive, optically active hydrophilic layer. Unsaturated fatty acids are particularly susceptible to oxidation due to the reactivity of the double bond with ozone.

A number of laboratory studies has used ozonolysis of oleic acid as a model system of fatty acids to investigate the chemistry of organic particle aging and its relation to aerosol hygroscopicity (Zahardis and Petrucci, 2007). However, significant absorption of water by oxidized oleic acid drops and films was only evident at very high ozone concentration (up to 500 ppm) (Asad et al., 2004; Hung and Ariya, 2007), and it has been argued that these conditions may not have been relevant for the atmosphere (Zahardis and Petrucci, 2007).

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

In this paper, we expose oleic acid (OA) and arachidonic acid (AR) aerosol particles to ozone and humidity under conditions as close as possible to ambient to establish a link between condensed phase alkene oxidation and hygroscopic growth. The goal was to determine the hygroscopic growth factor (GF) as function of ozone concentration and humidity and to relate the observed hygroscopic changes with the functional group composition of product particles. OA is a C18 monounsaturated fatty acid with a double bond at the C9 position, and AR is a polyunsaturated fatty acid with four double bonds at the C5, C8, C11 and C14 positions. Ozone attacks at the carbon-carbon double bonds, which leads to primary ozonides that then decompose into a range of products. For OA these are non-hygroscopic C9 acids, aldehydes and oligomers thereof (Zahradis and Petrucci, 2007). The AR-ozone reaction may lead to shorter chain species, including hygroscopic C3 and C5 dicarboxylic acids. The effect of water on condensed phase alkene oxidation has not been investigated so far, even though the reaction of the Criegee intermediates with water has been suggested to be significant in the gas phase (Hasson et al., 2001a). Product particles from both OA and AR oxidation are expected to represent the organic fraction of aged particles from emissions rich in fatty acids, such as in marine aerosol. For the purpose of these laboratory studies, the precursor particles are of sufficiently low volatility, and the product particles (for AR) are expected to contain a sufficient density of hygroscopic products.

## 2 Experimental

The aerosol particles were generated by passing a flow of nitrogen ( $1\text{ l min}^{-1}$ ) over a reservoir containing OA or AR in an oven kept at  $130^{\circ}\text{C}\pm 2^{\circ}\text{C}$  or  $160^{\circ}\text{C}\pm 2^{\circ}\text{C}$ , respectively, downstream of which OA or AR particles form by homogeneous nucleation by cooling to laboratory temperature. The particle number concentration and size distribution were continuously measured with a Scanning Mobility Particle Sizer system (SMPS). The resulting aerosol particles had a geometric mean diameter of 77 nm and 55 nm for OA and AR ( $\pm 2\%$  for both types), respectively, with a number concentration

### Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of  $5 \times 10^6$  particles  $\text{cm}^{-3}$  ( $\pm 30\%$  ( $1\sigma$ )). RH in the system was controlled from 0 to 95% at a precision of  $\pm 2\%$ .

Ozone was generated by irradiating a  $0.6 \text{ l min}^{-1}$  flow of a mixture of 40%  $\text{O}_2$  in  $\text{N}_2$  in a quartz tube with an ultra-violet lamp (Pen-Ray 3SC-9, UV Products Ltd., USA) and diluting it to a flow of  $1 \text{ l min}^{-1}$ . The aerosol and ozone flows were mixed together directly in front of the  $6.27 \text{ l}$  Teflon reactor kept at room temperature and with a residence time of 6 min. The concentration of ozone ( $0.5\text{--}2 \text{ ppm}$  with variations  $< 1\%$  during a 2 h time period) was measured with a photometric ozone analyzer (model ML 9810, Monitor Labs Inc, USA) downstream of the reactor in absence of aerosol. Ozone remained in excess with a depletion of at maximum 30%, if aerosol was present in the reactor, consistent with reported uptake kinetics. Ozone remaining at the exit of the reactor was scrubbed from the gas using a potassium iodide denuder to avoid secondary chemistry in the sampling devices.

We use an hygroscopicity tandem differential mobility analyzer (H-TDMA), to characterize the particles exiting the flow reactor (Sjogren et al., 2007; Weingartner et al., 2002). Hygroscopic growth, i.e., the change in diameter due to uptake of water, of particles with diameters between 20 and 250 nm was determined at room temperature and in the humidity range of 10% to 95% RH with an accuracy of  $0.1^\circ\text{C}$  and 1.6%, respectively. In the present experiments, the aerosol particles (flow rate:  $0.3 \text{ l min}^{-1}$ ) first entered a silica gel diffusion dryer in order to dry the sample to  $< 10\%$  RH at  $25^\circ\text{C}$ . The dry aerosol is then brought to equilibrium charge with a diffusion charger ( $^{85}\text{Kr}$ ) and fed into the first differential mobility analyser (DMA), where a narrow size range of dry aerosol (100 nm for OA and 68.5 nm for AR) is chosen. The monodispersed aerosol is then conditioned to a well-defined higher RH during 1 min. We have tested that 1 min. is sufficient to establish equilibrium between aerosol and water vapour. The aerosol particle diameter ( $D$ ) is then measured using the second DMA and a condensation particle counter (CPC, 3022A, TSI, USA). The GF is defined as the ratio of the humidified particle diameter ( $D$ ) to the dry particle diameter ( $D_0$ ). A humidogram describes the GF as a function of RH. Some substances show a hysteresis behaviour (forming

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

a meta-stable supersaturated solution). Therefore, in addition to the procedure described above, during which the aerosol is exposed to a certain RH from an initially dry condition, denoted as hydration case, the monodisperse aerosol is also exposed first to  $RH > 80\%$ , and then to the final RH, which is denoted as the dehydration case.

We use proton nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ), which is a suitable method to characterize complex mixtures of organic compounds, also with variable water content, in terms of its functional group composition (Decesari et al., 2000; Samburova et al., 2006). Filter samples were collected at the exit of the flow reactor during 2 h on a Teflon coated quartz fiber filter (TQFF) (PALLFLEX Membrane Filters, PALL Gelman, USA).  $^1\text{H-NMR}$  spectra were obtained at a frequency of 600 MHz on a model LA-400 spectrometer from JEOL (Tokyo, Japan) with a model FG-400 probe from Nanorac Cryogenics Corp. (Tokyo, Japan). Chemical shifts are reported in ppm. The filters were extracted with fully deuterated methyl sulfoxide- $d_6$  (DMSO- $d_6$ ) (99.9 atom % D, Aldrich), which allows observing the proton signals of the main functional groups directly in the spectra (Samburova et al., 2006). Dibromomethane ( $\text{CH}_2\text{Br}_2$ ) was added as internal quantification standard, as it gives a well resolved peak in the region of vinyl protons at 5.5 ppm. A detailed description of this procedure is given by Samburova et al. (2006). Carboxylic acid protons appeared as a group of peaks (14–10.5 ppm), well separated from aliphatic protons (0.5–2 ppm), which are in  $\beta$ -position and further away from an acid or carbonyl group. The unavoidable signals from DMSO- $d_6$  and trace amounts of water at 2.50 and 3.31 ppm, respectively, partially overlap with signals from aliphatic protons ( $-\text{CH}_n$ ) in  $\alpha$ -position to a carboxylic ( $\text{COOH}$ ) or carbonyl group. Only those in  $\beta$ -position or further away from oxygenated groups were included to calculate  $\text{COOH/CH}$  ratios.

### 3 Results and discussion

Figure 1a shows typical humidograms of processed and unprocessed OA aerosol. They show that the unprocessed OA particles take up only insignificant amounts of

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

water, with the GF of OA being 1.01 at 93% RH. This would correspond to about 2.5 formal monolayers of water on the surface or to about 1% volume fraction, consistent with the very low solubility of OA due to its long hydrophobic C<sub>18</sub>-chain. Similar results were observed on OA films and drops (Asad et al., 2004; Hung et al., 2005). A humidogram of OA aerosol processed by 1.84 ppm ozone (corresponding to an exposure of  $6.7 \times 10^{-4}$  atm s) and at 75% RH in the reactor is also shown in Figure 2a. The measured GF of the processed OA aerosol slightly increased to 1.03 at 93% RH as compared to unprocessed OA aerosol. We did not observe a significant change to this GF, when we performed the experiment at lower ozone concentration and lower humidity. As shown previously, the reaction of ozone with OA produces a variety of oxygenated products such as azelaic acid, nonanoic acid, 9-oxo-nonanoic acid and nonanal (Hung et al., 2005; Katrib et al., 2004; Moise and Rudich, 2002; Smith et al., 2002; Thornberry and Abbatt, 2004; Zahardis et al., 2005; Ziemann, 2005), some polymeric products (Hearn and Smith, 2005; Hung et al., 2005; Zahardis et al., 2005; Ziemann, 2005; Reynolds et al., 2006) and high-molecular-weight organic compounds (Hung et al., 2005; Zahardis et al., 2005; Ziemann, 2005). Even though some of the smaller products contain carboxylic acid groups that lead to a slightly increased water uptake, they are insoluble in water and not hygroscopic, as shown previously for pure azelaic acid (Andrews and Larson, 1993). In addition, the recent aerosol studies by Hearn and Smith (2005) and Katrib et al. (2005) suggest that these species are only minor reaction products.

In contrast, at ozone exposures orders of magnitude higher than in our study, Asad et al. (2004) (0.81 atm s) and Hung et al. (2005) (0.16 atm s) observed a significant increase of adsorbed water mass on an OA film and hygroscopic volume growth of deposited OA drops, respectively. Comparable to the hygroscopic behavior, Broekhuizen et al. (2004) measured an increased CCN activity at a supersaturation of 0.6% after ozone exposures higher than 0.14 atm s. These effects were probably due to further destruction of primary reaction products into smaller, more soluble organic species (Nepotchatykh and Ariya, 2002). Therefore, the previous experiments were only able

# Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to demonstrate increased water uptake after oxidation at ozone concentrations high enough to allow secondary chemistry leading to soluble products that will not be operative under atmospheric conditions (Zahardis and Petrucci, 2007). Our present data obtained at ozone concentrations of 0.5 to 2 ppm demonstrate that OA ozonolysis under atmospheric conditions is not leading to hygroscopic products.

As in the case of OA, the humidogram of unprocessed AR aerosol shows only very little size changes with relative humidity (Fig. 1b). When AR aerosol was processed with ozone under dry conditions and an ozone concentration of 0.5 or 2.0 ppm, corresponding to exposures of  $1.8 \times 10^{-4}$  atm s and  $6.7 \times 10^{-4}$  atm s, respectively, no increase in hygroscopic properties was observed, similar to the OA case. However, when the humidity in the reactor was set to 75%, a significantly increased hygroscopic growth was observed, e.g. at 1.84 ppm ozone, as shown in Fig. 1b. Here, the processed AR aerosol shows a monotonically increasing humidogram, and the observed GF at 95% RH in the H-TDMA is 1.09.

In contrast to the case of OA, ozonolysis of AR results in short C3-C6 multifunctional organic compounds that contain carboxylic and carbonyl groups, some of which are soluble and hygroscopic. For example malonic (MA) and glutaric acid (GA) have GFs 1.73 and 1.29 at 90% RH (Prenni et al., 2003), respectively. They have sufficiently low vapor pressures that they are expected to remain in the particulate phase (Makar, 2001). Nevertheless, we observed only significant changes in hygroscopicity in presence of water during ozonolysis at our moderate exposures, so that either water significantly accelerated the kinetics or changed the chemical mechanism. At high humidity (75%), the GF gradually increased with increasing ozone concentration (Fig. 2a). Similarly, the GF increased gradually with increasing humidity during ozonolysis at constant ozone exposure of  $6.7 \times 10^{-4}$  atm s (Fig. 2b).

Using  $^1\text{H-NMR}$ , the ratio of acid protons ( $-\text{COOH}$ ) to aliphatic ( $-\text{CH}_n$ ) protons in  $\beta$ -position and further away from the  $\text{COOH}$  groups was determined for each sample. The plot of this ratio (included in Fig. 2b) exhibits a gradual increase with increasing RH in the flow reactor from 0.055 to 0.12, in good correlation with hygroscopic GFs

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

measured online. It therefore seems that the increased hygroscopicity is related to an increased concentration of carboxylic acids in the particles with increasing humidity during ozonolysis, which indicates that the chemical mechanism under humid conditions promotes the formation of acids more than under dry conditions.

5 According to the “dry mechanism” of condensed phase alkene ozonolysis (see Fig. 3), the ozonolysis starts with the addition of ozone into the double bond and the formation of the primary ozonide, which is unstable and decomposes into an aldehyde and the Criegee Intermediate (CI). This CI, according to current thinking, could: (1) isomerize and form an acid group, (2) react with an aldehyde and form a secondary  
10 ozonide, (3) react with an acid group and form a hydroperoxide, (4) react with another CI and form a diperoxide. Depending on the matrix, these reactions can continue and lead to high-molecular weight compounds or further to oligomers.

The presence of water vapor during ozonolysis could influence this mechanism in several ways, e.g., by inhibiting or promoting isomerization or the reaction with an acid.  
15 Most likely, in analogy to the corresponding gas phase chemistry, water can react with a CI and form a hydrohydroxyperoxide (HHP, pathway (5)), that in turn decomposes heterogeneously to form either a carbonyl and  $\text{H}_2\text{O}_2$  or a carboxylic acid and  $\text{H}_2\text{O}$  (Hasson et al., 2001a; Horie et al., 1994). Therefore, this pathway (5) competes with (3), the reaction of CI with an acid. As our results show, the reaction with water seems  
20 to promote the formation of small water soluble acids, possibly at the expense of larger molecular weight complexes formed under dry conditions. We also note that even if in (5) only a small fraction decomposes into the acid and the majority into the aldehyde, the short aldehydes formed in AR ozonolysis are volatile and mostly lost to the gas phase, while the acids remain in the aerosol phase. This additionally increases the  
25 overall COOH content in the aerosol phase and especially the small dicarboxylic acid fraction, which are the most hygroscopic. The  $^1\text{H}$ -NMR measurements support the view that the presence of water shifted the reaction mechanism towards the production of carboxylic acids.

The  $^1\text{H}$ -NMR measurements of the COOH/CH ratio along with the range of expected

---

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

products allows to compare predicted and measured hygroscopic growth factors. For this, we assume that all new COOH contributing to the COOH/CH ratio of the product aerosol would be tied up in a 3:1 mixture of MA and GA and that the remainder of the products has a COOH/CH ratio similar to that of the parent AR. Taking into account a COOH/CH ratio of the parent AR of about 0.12 (at 83% RH in the reactor) and of a 3:1 mixture of MA and GA assumed as products of about 0.40, the measured COOH/CH ratio of the product aerosol would correspond to a mixture of 23.5% MA, 6.5% GA and 69.9% other products and AR, assuming that all these other products have a density of  $1 \text{ g cm}^{-3}$ . Using the Zdanovskii, Stokes, and Robinson (ZSR) method (Cruz and Pandis, 2000), we may predict the GF of the product aerosol by assuming ideal behaviour of solutes present. We take a GF of 1.73 for MA, 1.27 for GA, and 1.01 for the remaining fraction. This would result in a GF of 1.27 at 90% RH in the H-TDMA, which is much higher than the measured value of 1.07 obtained at 85% RH in the reactor and 90% in the H-TDMA. Note that this estimate is highly uncertain and it is likely that the growth behaviour is more complex. Nevertheless, it may indicate that also at high humidity, still about 75% of the newly formed acid groups are tied up in less hygroscopic compounds (monocarboxylic acids, oxoacids) or has participated in secondary reactions, e.g., with the CIs.

## 4 Conclusions and atmospheric implications

This study shows that a polyunsaturated fatty acid, such as AR, is a good model system to follow hygroscopic changes induced by oxidation of organic aerosol particles with an atmospherically relevant ozone exposure, and that water plays an important role in condensed phase alkene oxidation. Similar effects could not be demonstrated with a widely used proxy for such studies, OA, under these conditions. The ozone exposures used in the present experiments, namely from 0.5 to 2 ppm during the experimental reaction time (6 min) correspond to about 20 h exposure in the remote atmosphere. Under dry conditions, ozonolysis of condensed phase alkenes, either pure

### Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

or in mixtures with a protic matrix such as acids, is characterized by the formation of non-hygroscopic high molecular weight products. Under humid conditions, the reaction of water with the CIs might open a pathway for the formation of smaller acids that lead to more significant changes in hygroscopicity and possibly also in CCN activity. In spite of the nice correlation between the functional group analysis and the hygroscopic growth factors, this relation remains somewhat qualitative in character, as without more detailed product information a direct quantitative prediction of the growth factor is not possible. Thus the effect of water to provide a competing pathway during ozonolysis observed in this study is a reminder that the properties of a complex aerosol are not a simple superposition of the properties of its individual components.

*Acknowledgements.* The authors gratefully acknowledge T. Didenko (Laboratory of Physical Chemistry, ETH Zurich) for carrying out  $^1\text{H}$ -NMR measurements. This work was supported by the National Science Foundation Switzerland (grant n° 200021-100280).

## References

- Andrews, E. and Larson, S. M.: Effect of surfactant layers on the size changes of aerosol-particles as a function of relative-humidity, *Environ. Sci. Technol.*, 27, 857–865, 1993.
- Asad, A., Mmereki, B. T., and Donaldson, D. J.: Enhanced uptake of water by oxidatively processed oleic acid, *Atmos. Chem. Phys.*, 4, 2083–2089, 2004, <http://www.atmos-chem-phys.net/4/2083/2004/>.
- Cheng, Y., Li, S. M., Leithead, A., Brickell, P. C., and Leaitch, W. R.: Characterizations of cis-pinonic acid and n-fatty acids on fine aerosols in the lower fraser valley during pacific 2001 air quality study, *Atmos. Environ.*, 38, 5789–5800, 2004.
- Cruz, C. N. and Pandis, S. N.: Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol, *Environ. Sci. Technol.*, 34, 4313–4319, 2000.
- Decesari, S., Facchini, M. C., Fuzzi, S., and Tagliavini, E.: Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach, *J. Geophys. Res.-Atmos.*, 105, 1481–1489, 2000.
- Ellison, G. B., Tuck, A. F., and Vaida, V.: Atmospheric processing of organic aerosols, *J. Geophys. Res.-Atmos.*, 104, 11 633–11 641, 1999.

15661

ACPD

7, 15651–15668, 2007

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

- Hasson, A. S., Orzechowska, G., and Paulson, S. E.: Production of stabilized criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 1. Ethene, trans-2-butene, and 2,3-dimethyl-2-butene, *J. Geophys. Res.-Atmos.*, 106, 34 131–34 142, 2001a.
- Hearn, J. D., and Smith, G. D.: Measuring rates of reaction in supercooled organic particles with implications for atmospheric aerosol, *Phys. Chem. Chem. Phys.*, 7, 2549–2551, 2005.
- Horie, O., Neeb, P., Limbach, S., and Moortgat, G. K.: Formation of formic-acid and organic peroxides in the ozonolysis of ethene with added water-vapor, *Geophys. Res. Lett.*, 21, 1523–1526, 1994.
- Hung, H. M., Katrib, Y., and Martin, S. T.: Products and mechanisms of the reaction of oleic acid with ozone and nitrate radical, *J. Phys. Chem. A*, 109, 4517–4530, 2005.
- Hung, H. M. and Ariya, P.: Oxidation of oleic acid and oleic acid/sodium chloride(aq) mixture droplets with ozone: Changes of hygroscopicity and role of secondary reactions, *J. Phys. Chem. A*, 111, 620–632, 2007.
- Jacobson, M. C., Hansson, H. C., Noone, K. J., and Charlson, R. J.: Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, 38, 267–294, 2000.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: A review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005, <http://www.atmos-chem-phys.net/5/1053/2005/>.
- Katrib, Y., Martin, S. T., Hung, H. M., Rudich, Y., Zhang, H. Z., Slowik, J. G., Davidovits, P., Jayne, J. T., and Worsnop, D. R.: Products and mechanisms of ozone reactions with oleic acid for aerosol particles having core-shell morphologies, *J. Phys. Chem. A*, 108, 6686–6695, 2004.
- Kawamura, K. and Gagosian, R. B.: Implications of omega-oxocarboxylic acids in the remote marine atmosphere for photooxidation of unsaturated fatty-acids, *Nature*, 325, 330–332, 1987.
- Makar, P. A.: The estimation of organic gas vapour pressure, *Atmos. Environ.*, 35, 961–974, 2001.
- Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., and Suzuki, K.: Fatty acids in the marine atmosphere: Factors governing their concentrations and evaluation of organic films on sea-salt particles, *J. Geophys. Res.-Atmos.*, 107, 4325, doi:10.1029/2001JD001278, 2002.

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Moise, T. and Rudich, Y.: Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products, *J. Phys. Chem. A*, 106, 6469–6476, 2002.
- Nepotchatykh, O. V. and Ariya, P. A.: Degradation of dicarboxylic acids (c-2-c-9) upon liquid-phase reactions with o-3 and its atmospheric implications, *Environ. Sci. Technol.*, 36, 3265–3269, 2002.
- Novakov, T. and Penner, J. E.: Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, 365, 823–826, 1993.
- Oros, D. R. and Simoneit, B. R. T.: Identification and emission rates of molecular tracers in coal smoke particulate matter, *Fuel*, 79, 515–536, 2000.
- Oros, D. R. and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning part 1. Temperate climate conifers, *Appl. Geochem.*, 16, 1513–1544, 2001.
- Polzer, J. and Bachmann, K.: Determination of fatty-acids in atmospheric samples via gc/ms, *Fresen. J. Anal. Chem.*, 340, 555–559, 1991.
- Prenni, A. J., De Mott, P. J., and Kreidenweis, S. M.: Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids, *Atmos. Environ.*, 37, 4243–4251, 2003.
- Reynolds, J. C., Last, D. J., McGillen, M., Nijs, A., Horn, A. B., Percival, C., Carpenter, L. J., and Lewis, A. C.: Structural analysis of oligomeric molecules formed from the reaction products of oleic acid ozonolysis, *Environ. Sci. Technol.*, 40, 6674–6681, 2006.
- Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.: Sources of fine organic aerosol.1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, 25, 1112–1125, 1991.
- Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., and Simoneit, B. R. T.: Quantification of urban organic aerosols at a molecular-level - identification, abundance and seasonal-variation, *Atmospheric Environment Part A-General Topics*, 27, 1309–1330, 1993.
- Samburova, V., Didenko, T., Kunenkov, E., Emmenegger, C., Zenobi, R., and Kalberer, M.: Functional group analysis of high molecular weight compounds in the water-soluble fraction of organic aerosols, *Atmos. Environ.*, 41, 4703–4710, 2007.
- Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 1. C-1 through c-29 organic compounds from meat charbroiling, *Environ. Sci. Technol.*, 33, 1566–1577, 1999.
- Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: From air pollution to

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- climate change, John Wiley & Sons, Inc., New York, USA, 1998.
- Simoneit, B. R. T., and Mazurek, M. A.: Organic-matter of the troposphere.2. Natural background of biogenic lipid matter in aerosols over the rural western united-states, *Atmos. Environ.*, 16, 2139–2159, 1982.
- 5 Simoneit, B. R. T., Cox, R. E., and Standley, L. J.: Organic-matter of the troposphere.4. Lipids in harmattan aerosols of nigeria, *Atmos. Environ.*, 22, 983–1004, 1988.
- Sjogren, S., Gysel, M., Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A., Marcolli, C., Krieger, U. K., and Peter, T.: Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures,
- 10 *J. Aerosol Sci.*, 38, 157–171, 2007.
- Smith, G. D., Woods, E., DeForest, C. L., Baer, T., and Miller, R. E.: Reactive uptake of ozone by oleic acid aerosol particles: Application of single-particle mass spectrometry to heterogeneous reaction kinetics, *J. Phys. Chem. A*, 106, 8085–8095, 2002.
- Tervahattu, H., Hartonen, K., Kerminen, V. M., Kupiainen, K., Aarnio, P., Koskentalo, T., Tuck, A. F., and Vaida, V.: New evidence of an organic layer on marine aerosols, *J. Geophys. Res.-Atmos.*, 107, 4053, doi:10.1029/2000JD000282, 2002.
- Thornberry, T. and Abbatt, J. P. D.: Heterogeneous reaction of ozone with liquid unsaturated fatty acids: Detailed kinetics and gas-phase product studies, *Phys. Chem. Chem. Phys.*, 6, 84–93, 2004.
- 20 Wang, G. H., Kawamura, K., Watanabe, T., Lee, S. C., Ho, K. F., and Cao, J. J.: High loadings and source strengths of organic aerosols in china, *Geophys. Res. Lett.*, 33, L22801, doi:10.1029/2006GL027624, 2006.
- Weingartner, E., Gysel, M., and Baltensperger, U.: Hygroscopicity of aerosol particles at low temperatures. 1. New low-temperature h-tdma instrument: Setup and first applications, *Environ. Sci. Technol.*, 36, 55–62, 2002.
- 25 Zahardis, J., LaFranchi, B. W., and Petrucci, G. A.: Photoelectron resonance capture ionization-aerosol mass spectrometry of the ozonolysis products of oleic acid particles: Direct measure of higher molecular weight oxygenates, *J. Geophys. Res.-Atmos.*, 110, D08307, doi:10.1029/2004JD005336, 2005.
- 30 Zahardis, J. and Petrucci, G. A.: The oleic acid-ozone heterogeneous reaction system: Products, kinetics, secondary chemistry, and atmospheric implications of a model system – a review, *Atmos. Chem. Phys.*, 7, 1237–1274, 2007, <http://www.atmos-chem-phys.net/7/1237/2007/>.

## Fatty acid aerosol hygroscopicity induced by ozonolysis

O. Vesna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Ziemann, P. J.: Aerosol products, mechanisms, and kinetics of heterogeneous reactions of ozone with oleic acid in pure and mixed particles, Faraday Discuss., 130, 469–490, 2005

ACPD

7, 15651–15668, 2007

---

**Fatty acid aerosol  
hygroscopicity  
induced by  
ozonolysis**

O. Vesna et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

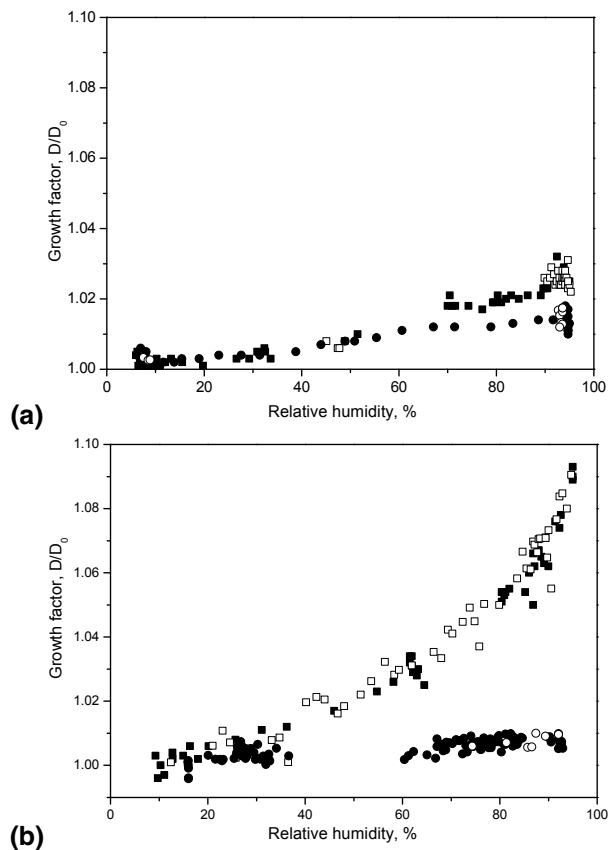
Printer-friendly Version

Interactive Discussion



**Fatty acid aerosol  
hygroscopicity  
induced by  
ozonolysis**

O. Vesna et al.

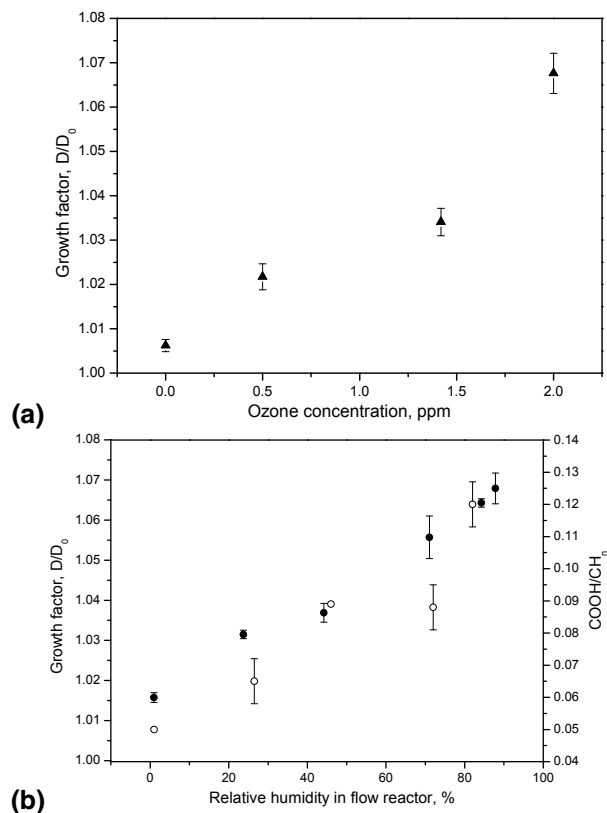


**Fig. 1.** Humidograms of OA (a) and AR (b) particles as function of RH. Squares and circles denote the GF of particles processed with 1.85 ppm ozone at 75% RH in the reactor and of unprocessed particles, respectively. Plain and empty symbols denote the hydration and dehydration modes, respectively.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Fatty acid aerosol  
hygroscopicity  
induced by  
ozonolysis**

O. Vesna et al.



**Fig. 2.** (a) Hygroscopicity of the AR particles as function of ozone concentration. The humidity in the aerosol flow reactor was 75% RH. (b) (○)  $\text{COOH}/\text{CH}_n$  ratio determined by  $^1\text{H}$ -NMR and (●) GFs of AR particles processed with ozone as function of the RH in the aerosol flow reactor. The initial ozone concentration was 1.84 ppm. H-TDMA measurements were corrected to 90% RH in both cases. The error bars represent the standard deviations.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

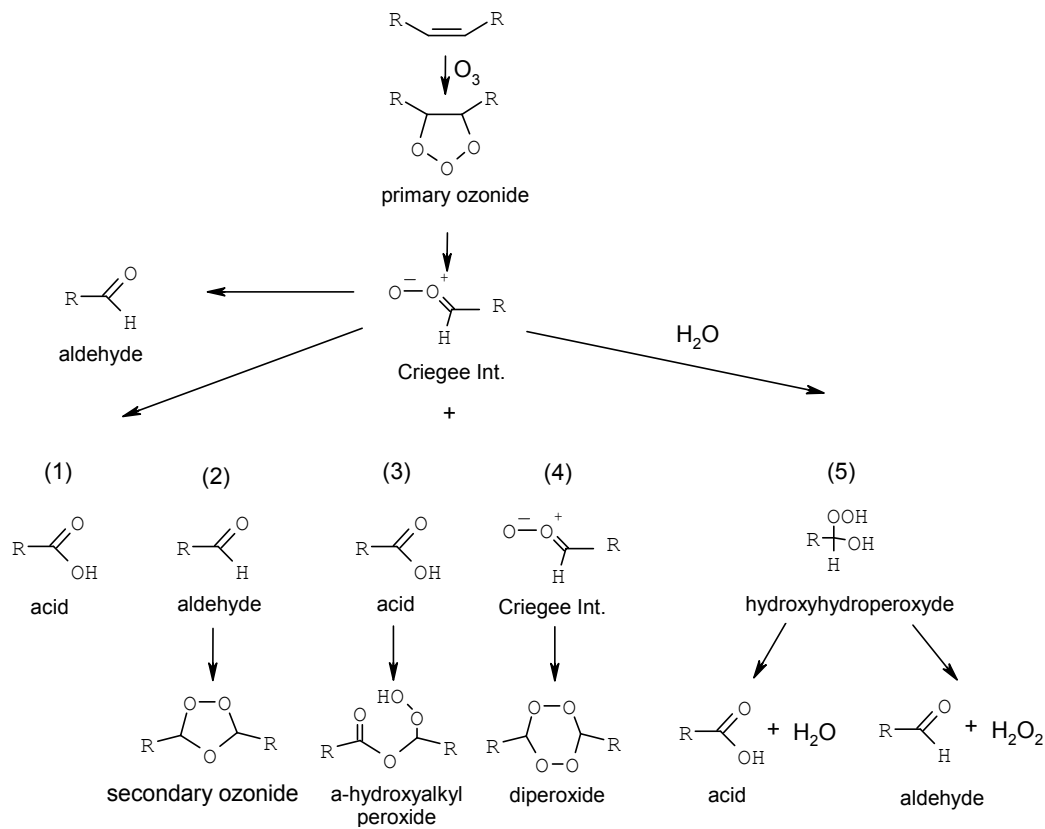
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Fatty acid aerosol  
hygroscopicity  
induced by  
ozonolysis**

O. Vesna et al.



**Fig. 3.** Proposed reaction mechanism for the ozonolysis of an unsaturated double bond. Formation pathways of acids, aldehydes, secondary ozonides, α-hydroxyalkyl peroxides and diperoxides in presence and absence of water.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion